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X-RAY AND ELECTRON DAMAGE OF CADMIUM SULFIDE

by K. W. Böer

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UNIVERSITY OF DELAWARE
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16. Abstract STUDIES OF X-RAY DAMAGE WERE PERFORMED ON CLASS I (GROSS-HOVIKOV) AND CLASS II CADMIUM SULFIDE CRYSTALS. CONSIDERABLE CHANGES OCCURRED IN CLASS I SPECTRAL DEPENDENCE PHOTOCURRENTS (SDP) AND THERMALLY STIMULATED CURRENTS (TSC) IN CLASS I CRYSTALS IRRADIATED AT 200 KEV X-RAYS AS COMPARED TO OBSERVATIONS OF 250 KEV IRRADIATED CLASS II CRYSTALS. THE OBSERVATIONS WERE ATTRIBUTED TO THE FACT THAT THE SURFACE IS ESPECIALLY SENSITIVE TO EITHER AMBIENT OR TO NEAR SURFACE LAYER RADIATION DAMAGE. THEREFORE, DAMAGE THRESHOLD MIGHT BE CONSIDERABLY LOWER FOR CLASS I CRYSTALS. STUDIES OF DAMAGE IN CLASS II CRYSTALS IRRADIATED AT 250 KEV SHOWED A TSC PEAK ATTRIBUTABLE TO SULFUR VACANCIES. HOWEVER, THE LIFETIME OF THE ELECTRONS INCREASED RATHER THAN DECREASED. MORE STUDIES ON THIS SYSTEM IS NEEDED IN ORDER TO CLARIFY THE DAMAGE MECHANISM.					
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X-RAY AND ELECTRON DAMAGE OF CADMIUM SULFIDE

By K. W. Böer

Physics Department, University of Delaware, Newark, Delaware

INTRODUCTION

The defect structure of CdS can strongly influence its photo-electrical properties. Both foreign (impurities) and intrinsic defects may be found. Impurity effects have been studied in some detail and are beginning to be understood (refs. 1-3). However, less progress has been made in understanding intrinsic defect effects in spite of the fact that a considerable amount of literature has appeared (refs. 4-18). This is in part due to the fact that most intrinsic defects are not found in concentrations above 10^{15} cm^{-3} at room temperature whereas impurities can be introduced in concentrations exceeding 10^{18} cm^{-3} -- that is, the highest concentrations of intrinsic defects are usually on the order of the trace impurity concentrations in a "pure" crystal. Another reason for the lack of progress in identifying intrinsic defects is that experimental results usually do not afford a means of distinguishing between point defects (e.g., vacancies, interstitials and substitutionals) and associated defects.

The intrinsic defect concentration can be changed by (1) shifting the stoichiometry by a heat treatment in the vapor of one of the components, (2) thermal damage, (3) radiation damage, and (4) self-diffusion studies using radioactive tracers. In the following work, the intrinsic defect structure was altered by using X-rays. Changes were detected by measuring the spectral dependence of photoconductivity (SDP) and thermally stimulated currents (TSC) before and after irradiation. In conjunction with, but independent from these particular measurements, CdS crystals were characterized from measurements of the photoconductivity in the band-gap region.

EXPERIMENTAL ARRANGEMENT

Apparatus

The crystals used in the tests reported herein were grown in our laboratory by the sublimation of CdS powder in an atmosphere of H_2S and N_2 (ref. 19). Platelets having a surface area of up to 1 cm^2 and a thickness of 50-100 μ meters could be obtained. Some crystals were intentionally doped with Cu while others were not intentionally doped.

Titanium-aluminum ohmic contacts (ref. 20) were evaporated onto the crystals. A single crystal was then placed on a mica sheet which lay on a

copper block (Figure 1). The crystal was held in place by two gold wires under tension that made electrical contact with the crystal electrodes. Thin copper wires connected the gold wires with instruments used to make electrical measurements. A 8.75-volt DC source, a micro micro ammeter and a recorder were connected in series with the crystal. A copper-constantan thermocouple was placed on a mica sheet on the copper block so that the temperature recorded by the thermocouple and the crystal temperature would be the same.

The crystal holder (which is situated on the end of a stainless steel cold finger) was mounted in an ultra-high vacuum system (Figure 2). Pressures as low as 10^{-10} torr were obtained using a VacSorb pump, a titanium sublimation pump and a 15 liter/second VacIon pump. A nude ionization gauge was used to measure the vacuum.

Crystals were illuminated using a high intensity Bausch and Lomb monochromator. The spectral half-width of the light falling on the crystal was approximately 30 Å. The monochromator was driven at a rate of 10 Å per minute for SDP measurements -- a rate sufficient enough to insure an equilibrium value of the photocurrent.

X-ray sources for the experiments were obtained at the Frankford Arsenal in Philadelphia and at Langley Research Center in Hampton, Virginia. An anti-cathode of high atomic number (either tungsten or gold) was used to convert electrons into X-rays. The maximum energy used was 250 keV. Exposure times ranged from 1 hour to 5 hours.

Procedure

Crystals were chosen that showed at least moderate photosensitivity. Vacuum was obtained in the vacuum chamber using the VacSorb pump, the titanium sublimation pump and the VacIon pump in succession. Care was taken to prevent ion bombardment of the crystal when the VacIon pump was activated. (This was done by using the titanium sublimation pump to get to a vacuum of about 10^{-5} torr before the VacIon pump was turned on.) Vacuums below 10^{-7} torr were easily obtained. To obtain lower vacuums, the vacuum system was baked while making sure that the crystal temperature did not exceed 50° C. (It is known that temperatures in excess of 100° C can cause substantial changes in crystal behavior, ref. 21.) After this treatment, the pressure fell to approximately 10^{-9} torr.

A series of SDP at room and liquid nitrogen temperatures and TSC measurements were performed to check reproducibility. Then the crystals were irradiated at room temperature with X-rays having a peak energy of either 200 keV or 250 keV (for further description see experimental results). Immediately following irradiation the crystals were cooled to liquid nitro-

gen temperature in order to freeze-in any defects created. Then, after a certain period of time not in excess of 2 hours, an SDP measurement at liquid nitrogen temperature was made. Following the SDP, a TSC curve was obtained. In some cases, an SDP measurement at room temperature was subsequently made. The measurements of the SDP and TSC were repeated several days after irradiation. The crystal was maintained at room temperature and in the dark during this period.

In conjunction with the above experiments, detailed photoconductivity and luminescence measurements were made on CdS crystals in order to characterize them (ref. 21) (i.e., to determine whether the crystals being tested were Class I or Class II according to the Gross-Novikov scheme, ref. 22). Measurements were made at room and liquid nitrogen temperature in a high vacuum (approximately 10^{-8} - 10^{-9} torr). The crystals were heat treated, and changes in the SDP and luminescence were observed.

EXPERIMENTAL RESULTS

Crystal Characterization and the Effect of Heat Treatment

Crystals that showed a great deal of green edge luminescence centered around 5200 Å were tested (Figure 3, curve 1). By photoconductivity measurements in 4800 - 4900 Å region at liquid nitrogen temperature, it was found that the crystals were Class I according to the Gross-Novikov classification scheme (ref. 22) (Figure 4). That is, at 78° K, Class I crystals exhibited a coincidence in energy of the maxima of photoconductivity with the maxima of the optical absorption constant. In Figure 4, A_1 and B_1 stand for the ground state excitons arising from two of the valence bands in CdS causing the optical absorption maxima. (The detailed photoconduction structure is not seen at room temperature). At room temperature, Class I crystals exhibited a behavior in the SDP different from Class II crystals. Class I crystals are characterized by a shoulder occurring at ~ 4800 Å in the room temperature SDP, whereas Class II crystals have a peak at 5180 Å with decreasing photoconductivity as one moves away from the peak on either side (Figure 5). (It is also possible to find crystals that have both a peak and a shoulder in the SDP at room temperature.)

When the crystals were heat treated for 5 minutes at 200° C, the green edge luminescence decreased sharply while the luminescence below 4900 Å increased slightly (Figure 3, curve 2). The SDP at both room and liquid nitrogen temperature increased drastically, and the shape of the curve changed completely (Figure 6). Maxima in the SDP appeared where minima were previously observed. Therefore, the crystal had changed to type II after heat treatment at 200° C.

Effect of X-radiation

The first investigations were made with Class II crystals as these were the ones that were made at the University of Delaware. Recently, the crystals that have usually been grown have been Class I crystals. Consequently, the crystals that were investigated first (C-1, C-2, C-3) were Class II crystals and C-4 was essentially a Class I crystal. One Type II crystal (C-1) was irradiated in a vacuum of $\sim 10^{-8}$ torr for five hours at Langley Research Center with X-rays having a maximum energy of 250 keV. TSC curves were obtained before and after irradiation (Figure 7). The damage was annealed by subjecting the crystal to a 100° C temperature for one hour. A subsequent radiation at 250 keV for 5 hours produced similar damage in the crystal. Due to degraded contacts, no further experiments were made on crystal C-1.

A second crystal (C-2) was exposed to 200 keV (maximum) X-rays for one hour. No changes in the SDP or TSC were observed. It is believed that the crystal was not exposed to a large enough radiation dose.

A third crystal (C-3) was exposed to 250 keV (maximum) X-rays for 4 hours with the ambient pressure being 10^{-7} torr. Measurement of the room temperature SDP prior to irradiation indicated that the crystal was Type II. Changes were observed in both the SDP at liquid nitrogen temperature and the TSC (Figures 8,9). A few days after irradiation, the SDP had returned to its pre-irradiation condition while the TSC had dropped back somewhat to its pre-irradiation condition. (The crystal was kept in the dark at room temperature between measurements.) Within two weeks the TSC returned to its pre-irradiation condition.

A fourth crystal (C-4) was irradiated with 200 keV (maximum) X-rays for 4 hours with the ambient pressure being about 10^{-6} torr. Prior SDP measures had indicated that the crystal was intermediate to Class I and Class II -- that is, it showed both a shoulder and a peak in the SDP at room temperature. Substantial changes in the SDP were observed at liquid nitrogen temperature (Figure 10). The whole curve shifted upwards with marked changes in both the extrinsic and intrinsic ranges. In addition, the crystal became sensitive to red light in the 6000 - 6500 Å region, whereas before the crystal showed no sensitivity. After storage at room temperature for 5 days, the SDP returned towards its pre-irradiated condition. After six more weeks at room temperature the crystal was much like its virgin condition except the "dark" current had decreased by an order of magnitude. Also, there was no sensitivity in the 6000 - 6500 Å region.

Room temperature SDP measurements showed trends much like the measurements at liquid nitrogen temperature (Figure 11). They also indicated that no change in crystal class occurred.

TSC measurements also changed markedly (Figure 12). They also exhibited the same tendencies as the SDP measurements. After approximately seven weeks the pre- and post-irradiation curves were nearly the same. No definite structure was observed in the TSC curves immediately after irradiation although very definite structure (at about 225° K) was observed before irradiation.

DISCUSSION

In order to discuss these results, it is necessary to consider the influence and significance of the following: crystal type, pressure during irradiation and threshold for damage.

Crystal Type

As mentioned previously, there are two basic CdS crystal types that can be classified. Class I crystals have associated with them green edge luminescence and a shoulder in the SDP at room temperature. (The shoulder is not seen at liquid nitrogen temperature.) Also, recent measurements (ref. 23) indicate that in Class I crystals oxygen adsorbed at the surface plays an important role in the photoelectrical properties. As a result of oxygen desorption and the diffusion of Cd in the bulk (or possibly partial Cd evaporation) at high temperatures Class I crystals can be changed to Class II crystals.

It has been suggested that the photocurrent in both the intrinsic and extrinsic range in Class I crystals is essentially carried by a thin near surface layer of at most 10^{-5} cm thickness (ref. 23). Adsorbed oxygen partially compensates the accumulation layer produced by excess cadmium in this surface layer. When the oxygen is desorbed, an electronic sensitization occurs, thereby causing an increase in photo- and dark-current. With a crystal temperature greater than 500° K, the crystal is converted into Class II.

Class II crystals have a photosensitivity not solely due to the surface -- possibly because of Cd diffusion into the bulk and partial Cd evaporation. For intrinsic excitation, the photocurrent is carried in the near-surface layer. Recombination of carriers can take place at the surface (the time necessary for the majority of the carriers to reach the surface by random walk is less than the lifetime of free majority and minority carriers). For extrinsic excitation, recombination at the surface is not likely since the random walk time is greater than the lifetime of free majority and minority carriers. It may be noted that oxygen desorption from Class II crystals shows only a small influence on the photoconductance.

Radiation Damage and the Effect of Ambient Pressure

It is possible to discuss radiation damage of CdS within a general scheme once the classification of CdS crystals has been clarified. It is necessary to consider the two classes separately since the region of the crystal (i.e., the near surface layer or the bulk) involved in photoelectric properties is quite different for the two crystal classes.

In previous measurements by O'Connell (ref. 18) a threshold for damage was found to be approximately 300 keV in a vacuum of 10^{-9} torr. Class II crystals were tested. A decrease in electron lifetime was observed. (This result -- which is contrary to the present result -- may be due to the fact that O'Connell's crystals were not virgin crystals. He exposed them to a temperature of as much as 180° C before irradiation.) In the present experiment on Class II crystals, it was found that the damage threshold was less than 250 keV for an ambient pressure of $\sim 10^{-8}$ torr. Since the SDP curve made a parallel shift upward as a result of the radiation, it is believed that a decrease in recombination center density occurred although an increase in hole traps is a possibility, thereby resulting in a longer electron lifetime. The TSC curves for Class II crystals showed an increase in levels around 300° K in agreement with O'Connell. These levels were attributed to an increase in sulfur vacancies by him. (It should be noted that a general increase in the TSC occurred over the temperature range. However, the change at 300° K was more than a parallel shift).

The result for the damage threshold is considerably higher than that found by Kulp and Kelley (ref. 7). There are two possible reasons for this. One, the X-rays that were used were distributed in energy and not monochromatic. Relatively few photons had an energy near the maximum accelerating potential of the X-ray machine -- that is, the largest number of photons had energies significantly less than the maximum. As a consequence, the dose received by the crystal at a given energy becomes important. Secondly, it is possible that the ambient pressure in the vacuum chamber had a significant effect on the threshold. Residual gases might be ionized and impact the surface of the crystal thereby causing structural changes. A much lower ambient pressure would eliminate this possibility. Kulp and Kelley irradiated their samples with electrons in a vacuum of 10^{-5} torr whereas O'Connell used X-rays in a 10^{-9} torr vacuum. In the present case vacuums from 10^{-7} torr to 10^{-8} torr were used in Class II crystals.

It is noteworthy that Kulp and Kelley were able to produce green edge luminescence in their crystals above their threshold value (also, they produced red luminescence). Green edge luminescence appears to be connected with the near-surface region and not the bulk (refs. 21 and 24). Therefore, Kulp and Kelley apparently caused changes in the near surface region -- which may indicate that the ambient pressure was a significant factor in the damage. (It should be noted that at ~ 100 keV electrons penetrate considerably further into the crystal than 10^{-5} cm, the thickness of the near

surface region.) Damage to the near surface region may require a considerably lower threshold than would be the case for the bulk.

More recent measurements by Im and Bube (ref. 25) using electrons in an unreported vacuum have indicated changes in photoelectronic properties at energies as low as 75 keV. However, the crystals that were used had been treated in sulfur vapor prior to testing. Im and Bube suggest that the radiation induced changes observed may be due to changes in interstitial sulfur that was present as a result of the sulfur treatment. They also report an increase in electron lifetime at the lower radiation energies ($E_{\text{electron}} \leq 250$ keV), a result which was obtained in the present experiment. At an energy of 400 keV, they noted a substantial decrease in the electron lifetime which they suggest might be due to both Cd and S being displaced from their lattice positions.

The situation with Class I crystals appears to be quite different from Class II crystals regarding the damage threshold. The present results indicate that the damage threshold is below 200 keV. (Results of others indicate that the threshold may be much lower. These will be discussed later.) Considerable upward shifts were noticeable in both the intrinsic and extrinsic range although the peak current did not change too much. The shift in the extrinsic region was greater than that in the intrinsic region. Also, a sensitivity to 6000 - 6500 Å illumination appeared that was previously lacking. TSC curves indicated an over all increase of electrons in traps; no defined trapping level appeared as a result of irradiation. It is not immediately apparent as to what is responsible for the observed changes since the near surface layer is important in this class of crystal. However, it is apparent that the lifetime of electrons was increased.

Because the near surface layer is particularly important in Class I crystals, any change in the surface layer might be particularly apparent. For example, residual gas in the vacuum chamber that might be ionized by the incident radiation could cause substantial changes in the photoelectronic properties of the crystal. Kulp and Kelley (ref. 7) reported that the green edge luminescence could be made to disappear by bombarding crystals with electrons having energies ranging from 3 keV to 200 keV. As stated previously, their pressure was 10^{-5} torr during irradiation. It is conceivable that the use of X-rays and much lower ambient pressures might result in higher energies being necessary to cause damage to the crystal. Therefore, further studies of Class I crystals are necessary to find out the damage threshold, the effect of ambient pressure and the defects that are responsible for the substantial changes observed.

SUMMARY

It has been found that there are basically two different classes of CdS crystals that apparently exhibit substantially different behavior as a

result of X-radiation. Class I crystals (Gross-Novikov classification) have the photocurrent carried by a thin near-surface region (10^{-5} cm) which is presumably Cd rich. The resulting accumulation layer is partially compensated by oxygen. Considerable changes in both the SDP and TSC curves occurred as a result of irradiation with 200 keV X-rays (maximum). These changes were greater than changes observed in Class II crystals irradiated at 250 keV. This may be attributable to the fact that the surface is especially sensitive either to ambient ions bombarding the surface or to actual radiation damage in the near surface layer. It is suggested that the damage threshold might be considerably lower for Class I crystals because of this surface sensitivity.

In Class II crystals, the photocurrent is carried in the bulk for extrinsic excitation and in the surface for intrinsic excitation. SDP and TSC measurements showed changes as a result of 250 keV X-radiation although no changes were observed at 200 keV. An increase in a TSC peak at 300° K (presumably attributable to sulfur vacancies) was observed in agreement with previous measurements of O'Connell. However, the lifetime of electrons increased rather than decreased. Again, the effect of ambient ions bombarding the surface of the crystal might be important regarding the damage threshold.

Although progress has been made in clarifying the picture regarding radiation damage in CdS crystals, it is clear that more information needs to be obtained. In particular, more information is needed on the respective damage thresholds in Class I and Class II crystals in addition to the defects that result from the radiation.

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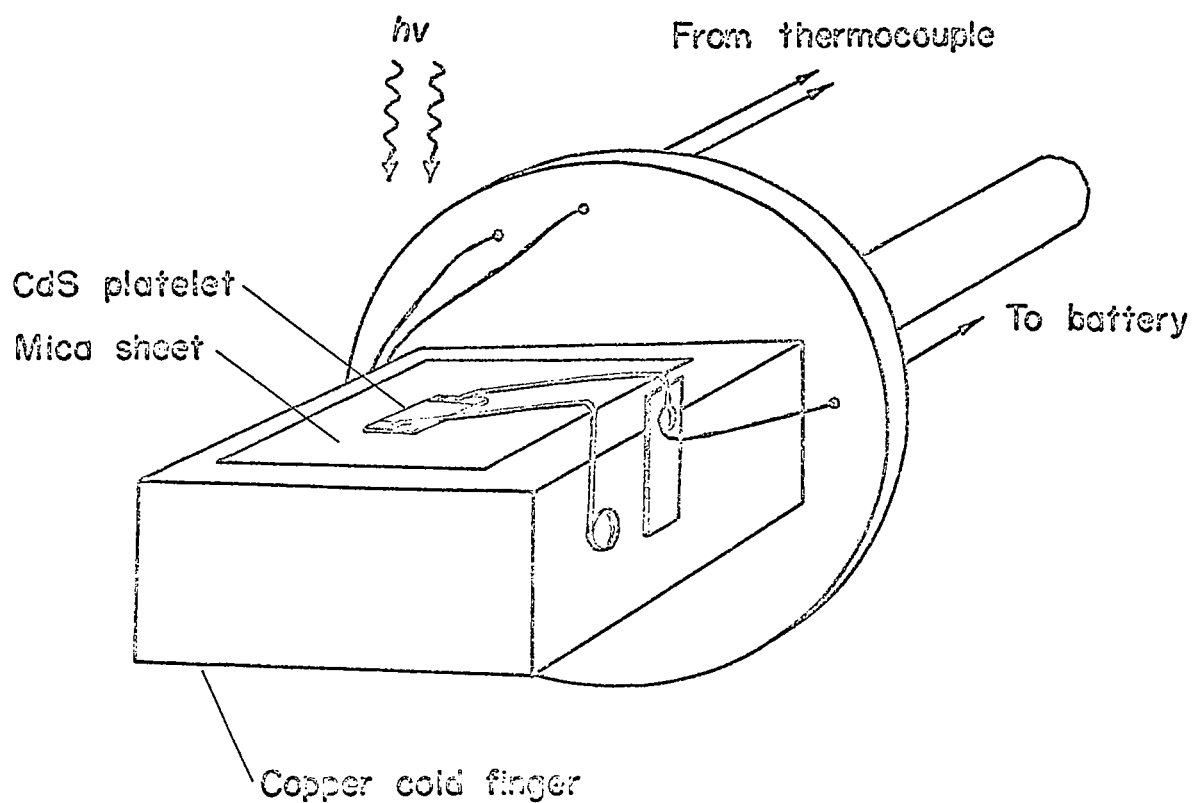


FIGURE 1: Enlarged view showing CdS crystal mounted on cold finger. A copper shield that has a small hole in it to allow for the illumination of the crystal fits over the finger.

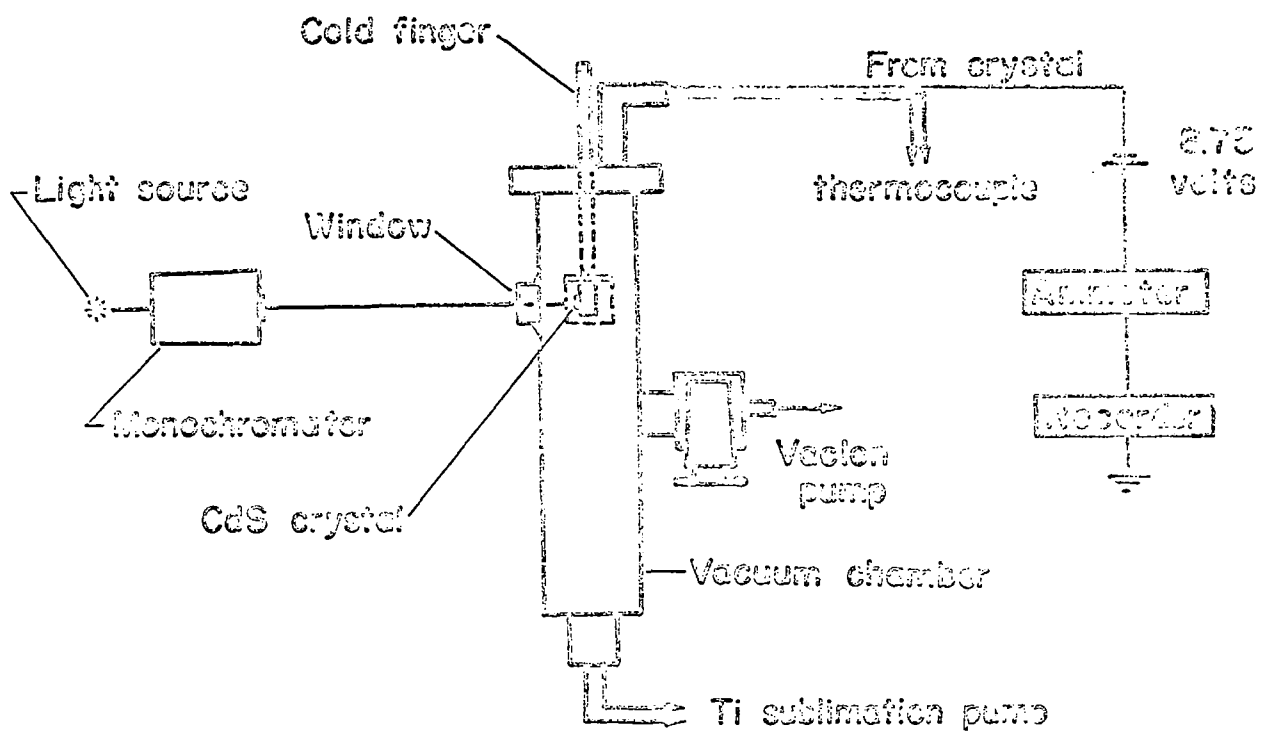


FIGURE 2: Experimental apparatus

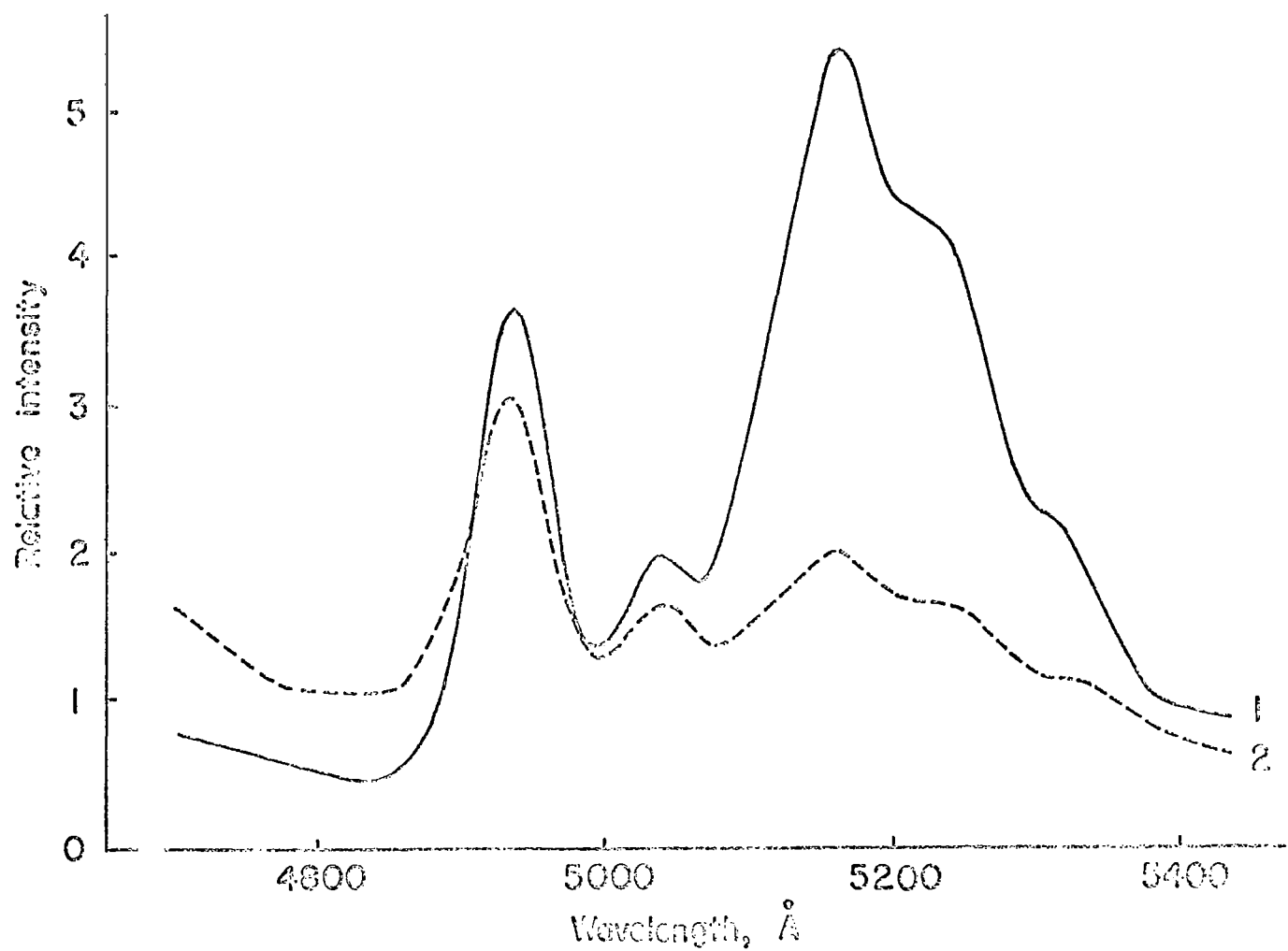


FIGURE 3: Luminescence spectra of CdS at 78° K and the effect of a slight heat treatment. Curve 1: Untreated crystal. Curve 2: After heat treatment at 200° C. (From reference 21).

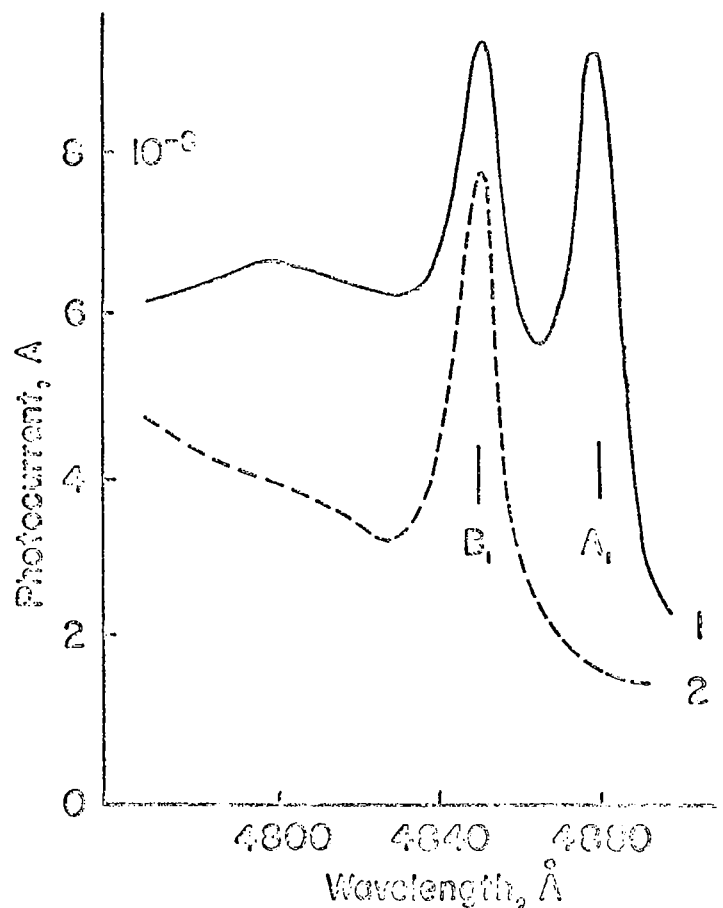


FIGURE 4: Spectral distribution of the photoconductivity for the untreated crystal at 78° K. Curve 1: $E \perp C$ - axis. Curve 2: $E \parallel C$ - axis. A_1 and B_1 represent the energy positions of the A_1 and B_1 excitons. (From reference 21).

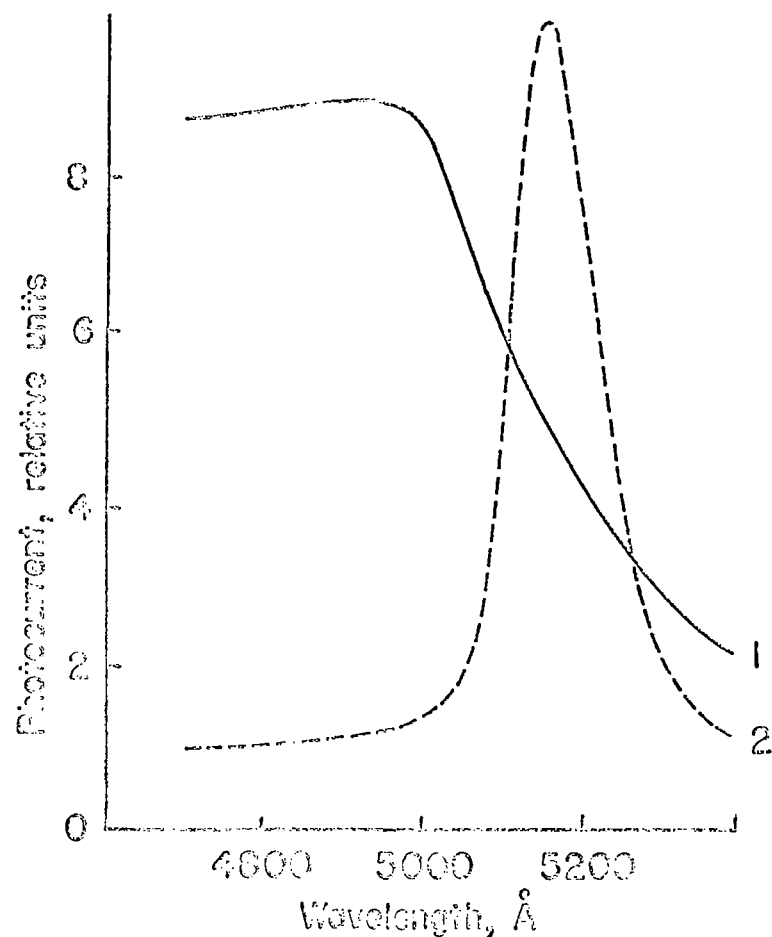


FIGURE 5: Spectral distribution of the photoconductivity at room temperature. Curve 1: Class I crystal. Curve 2: Class II crystal. (From reference 21).

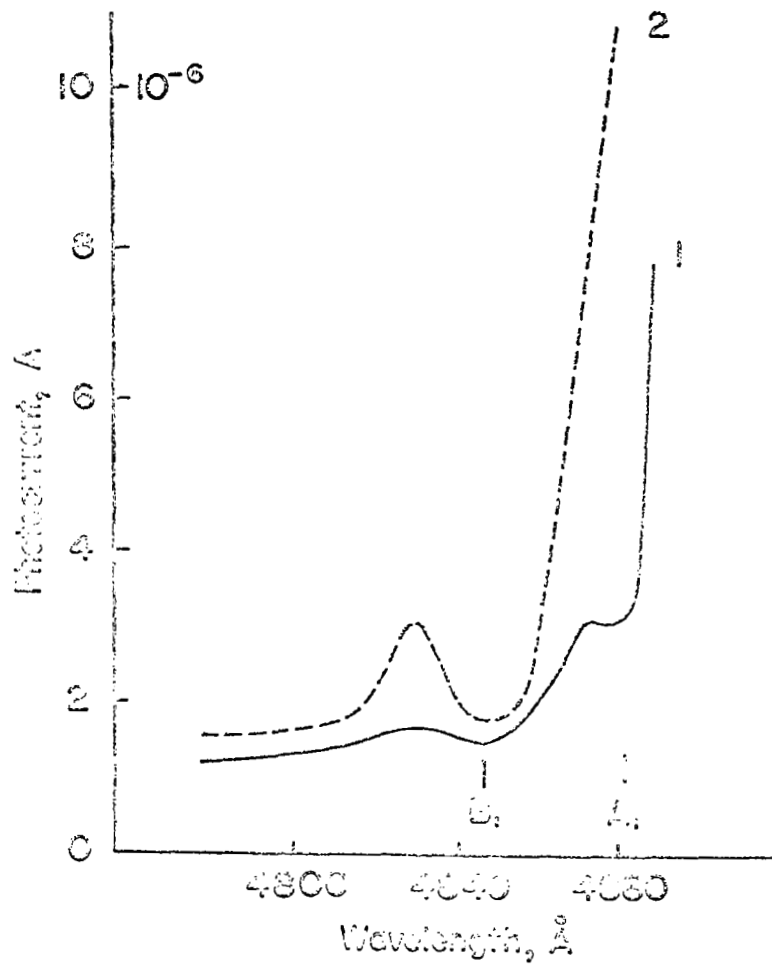


FIGURE 6: Spectral distribution of the photoconductivity at 78° K after 200° C heat treatment. Curve 1: $E \perp C$ - axis. Curve 2: $E \parallel C$ - axis. A_1 and B_1 represent the energy position of the A_1 and B_1 excitons. (From reference 21).

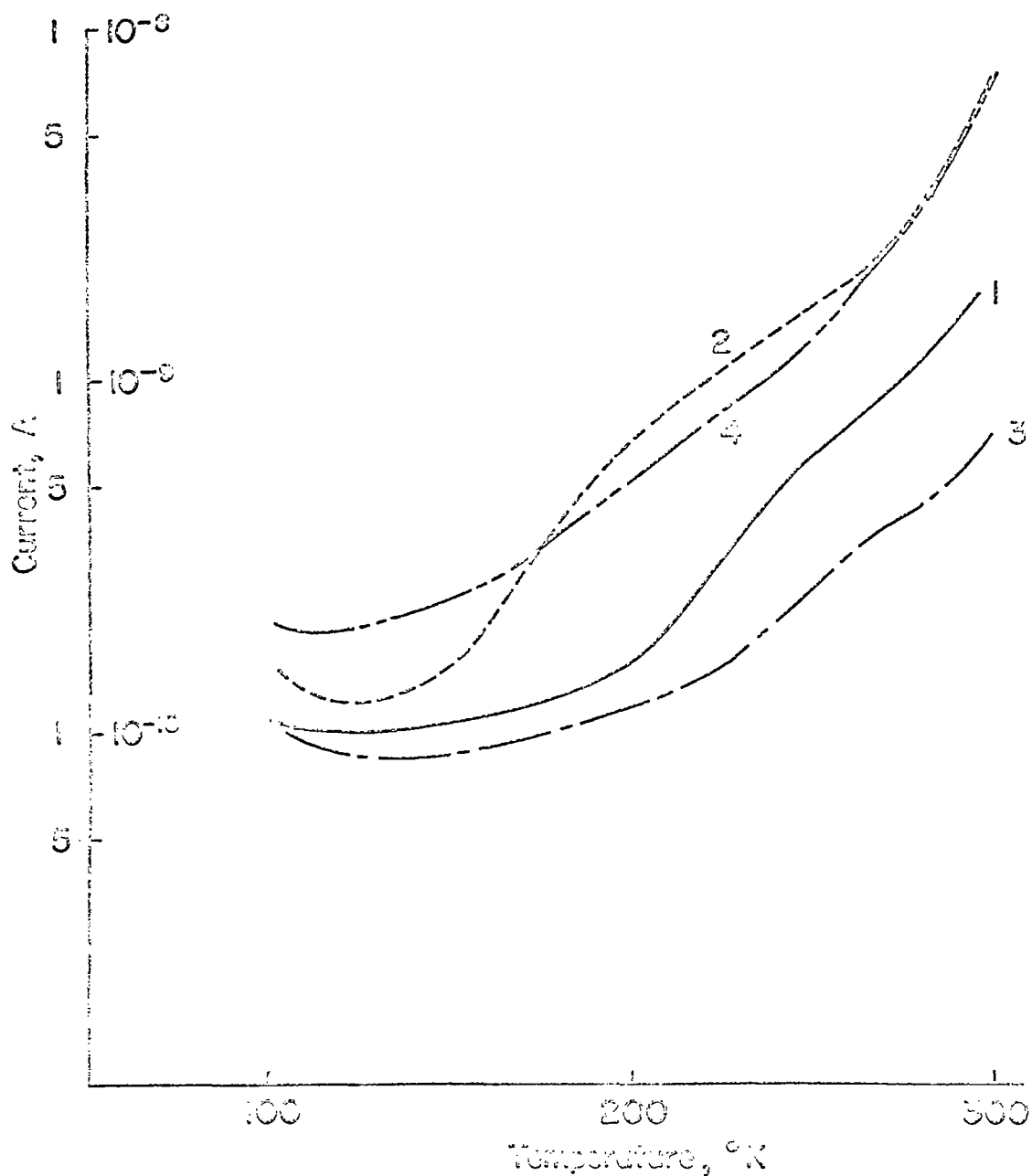


FIGURE 7: Thermally stimulated currents obtained before and after X-irradiation at room temperature and 250 keV for 5 hours from crystal C-1. Curve 1: Before irradiation. Curve 2: After first irradiation. Curve 3: After annealing at 100° C. Curve 4: After second irradiation.

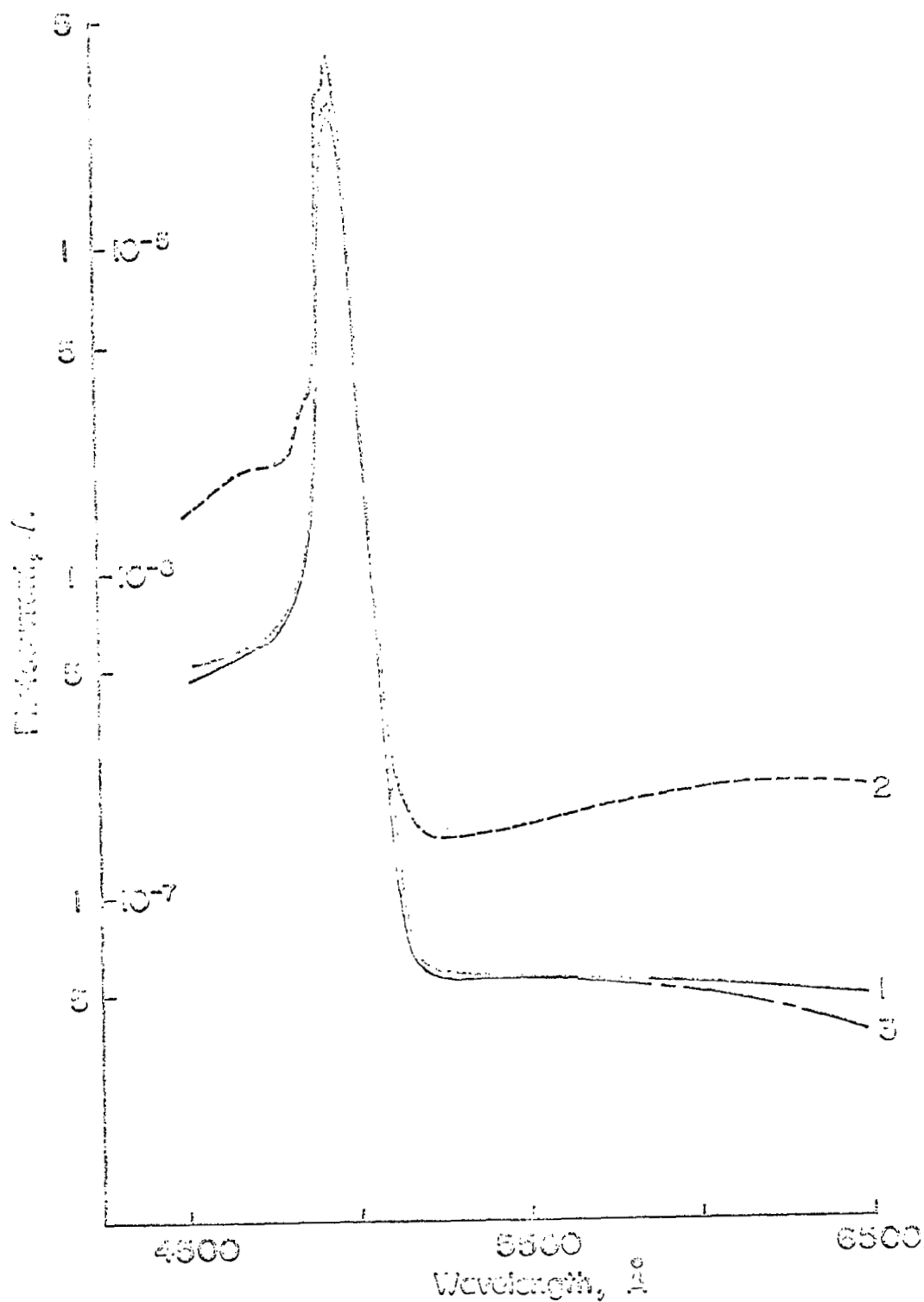


FIGURE 6: Spectral distribution of the photoconductivity at liquid nitrogen temperature before and after X-irradiation at 250 keV from crystal C-3. Curve 1: Before irradiation. Curve 2: After irradiation. Curve 3: After 5 days at room temperature.

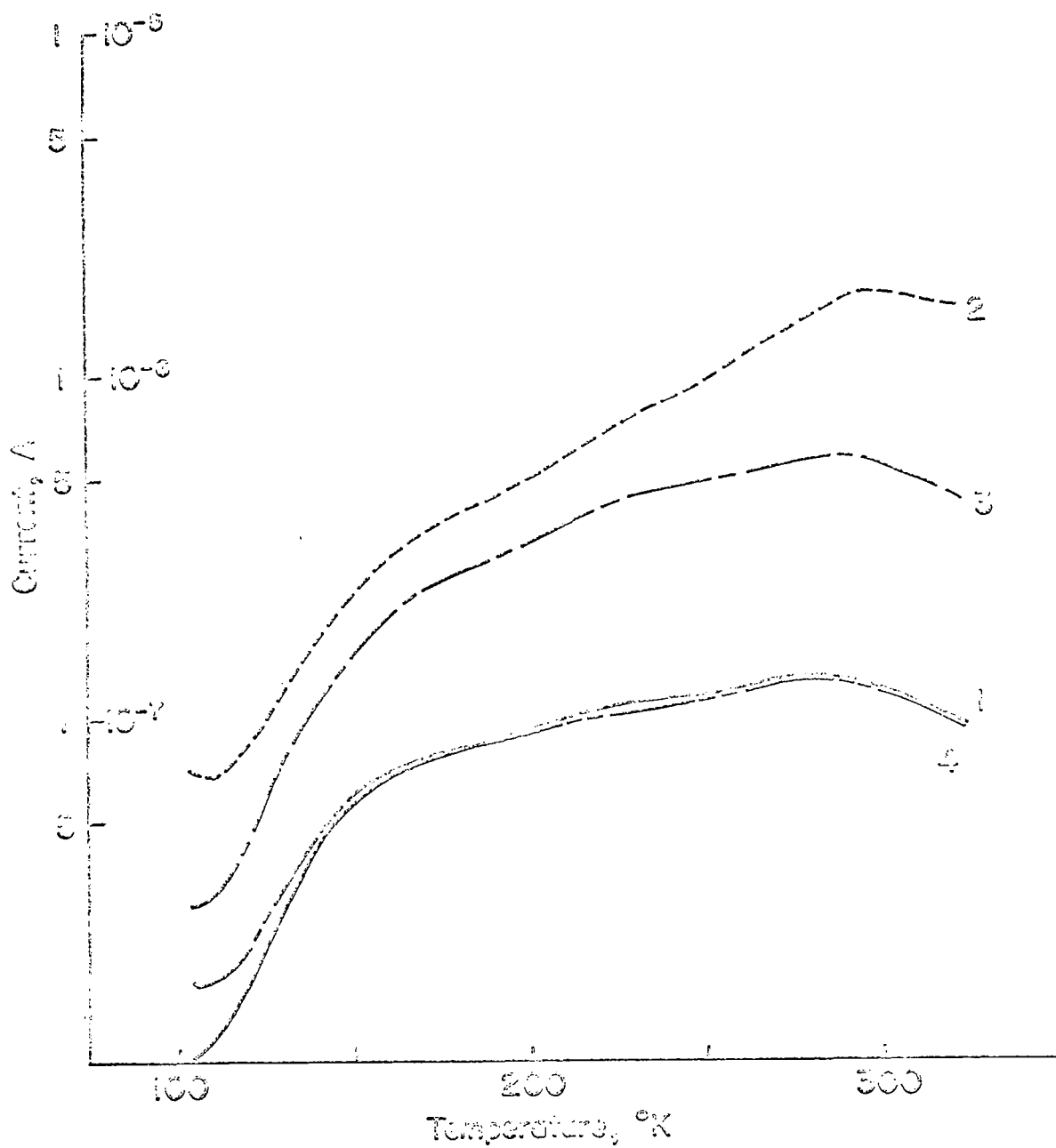


FIGURE 9: Thermally stimulated currents before and after X-irradiation at 250 keV from crystal C-3. Curve 1: Before irradiation. Curve 2: After irradiation. Curve 3: After 5 days at room temperature.

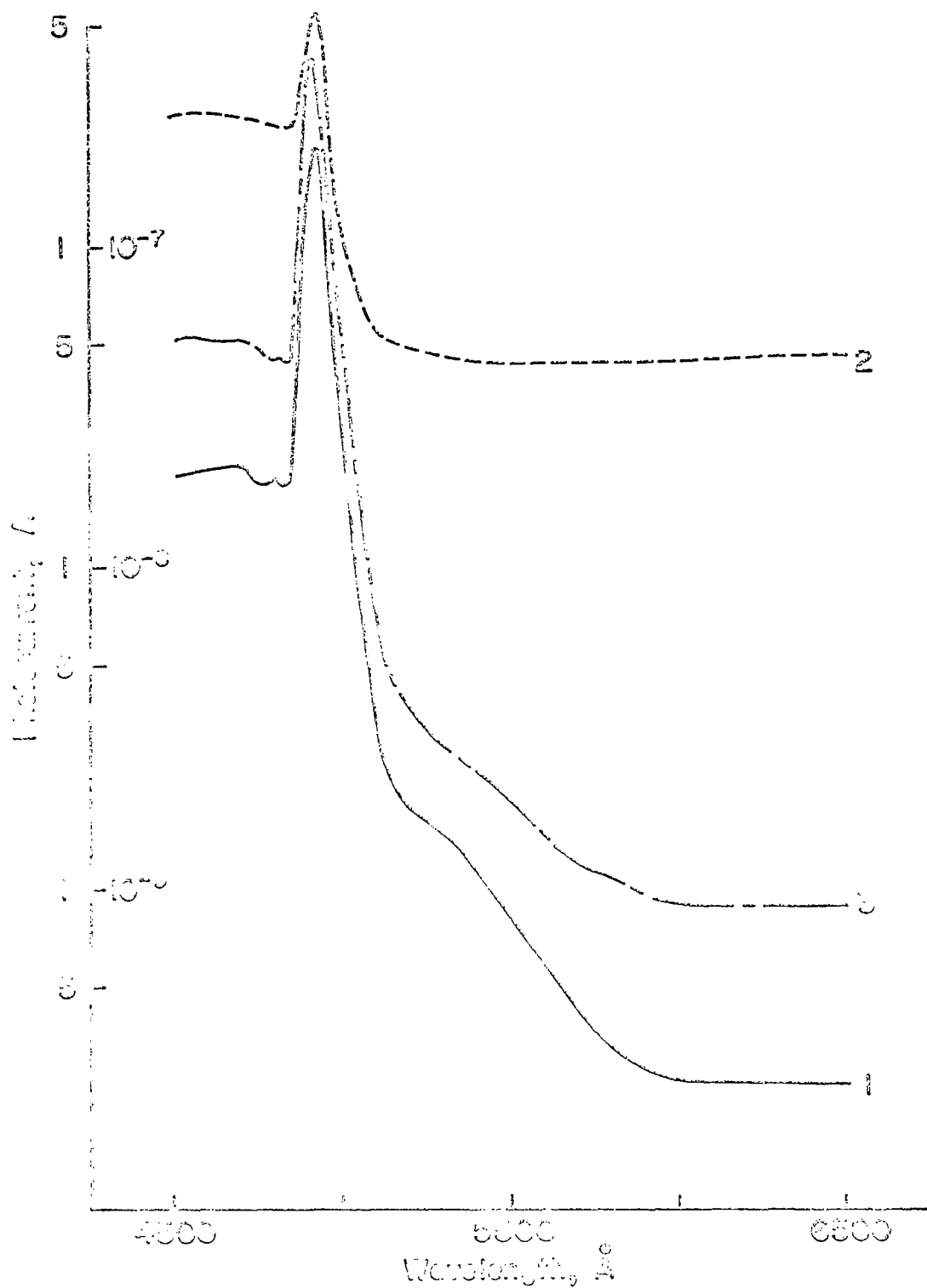


FIGURE 10: Spectral distribution of the photoconductivity at liquid nitrogen temperature before and after X-irradiation, at 200 keV for crystal C-4. Curve 1: Before irradiation. Curve 2: After irradiation. Curve 3: After 6 days at room temperature.

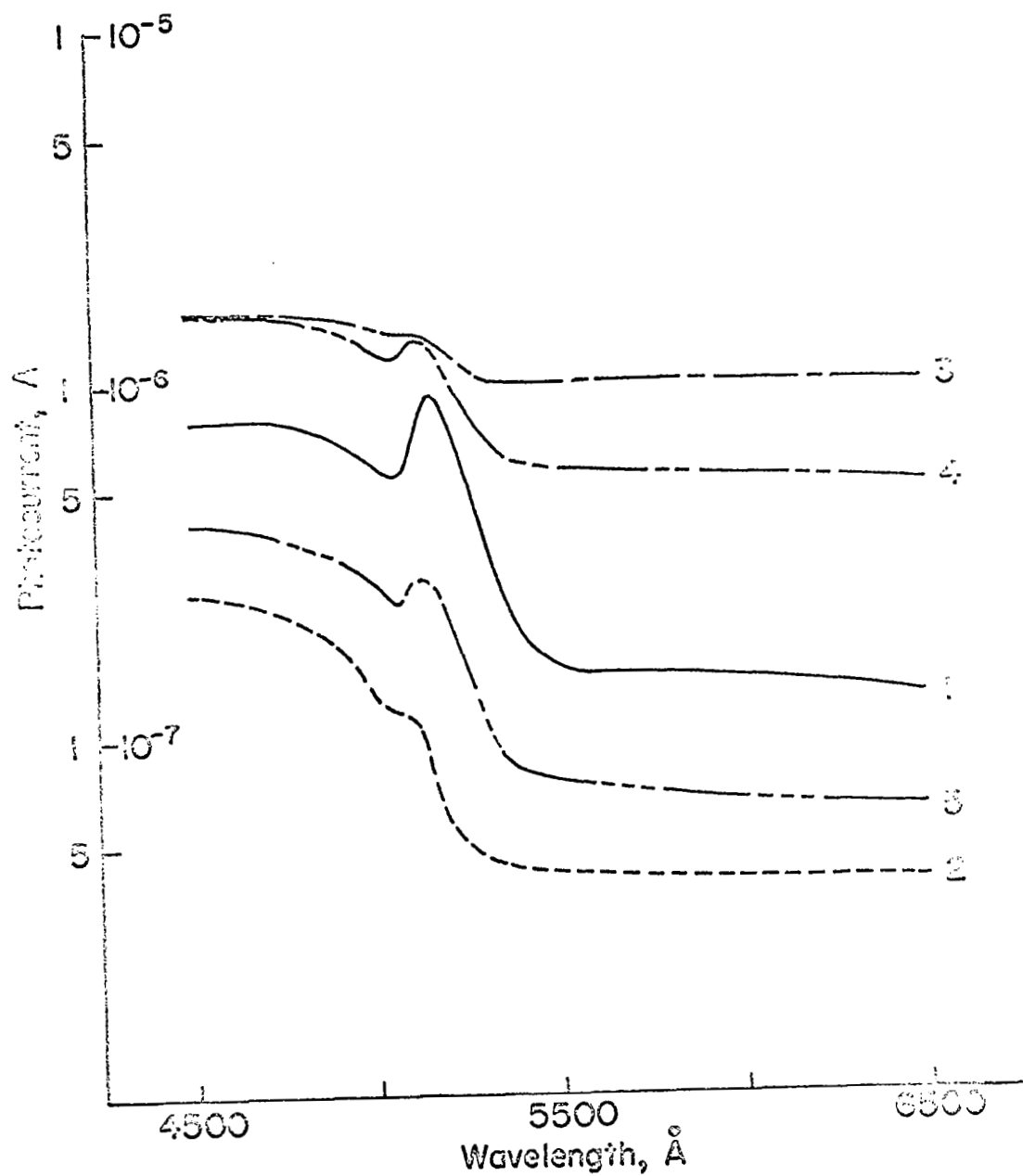


FIGURE 11: Spectral dependence of the photoconductivity at room temperature before and after X-irradiation at 200 keV for crystal C-4. Curve 1: Before irradiation. Curve 2: Before irradiation and after 100° C heat treatment. Curve 3: After irradiation. Curve 4: After 4 days at room temperature. Curve 5: Two months after irradiation.

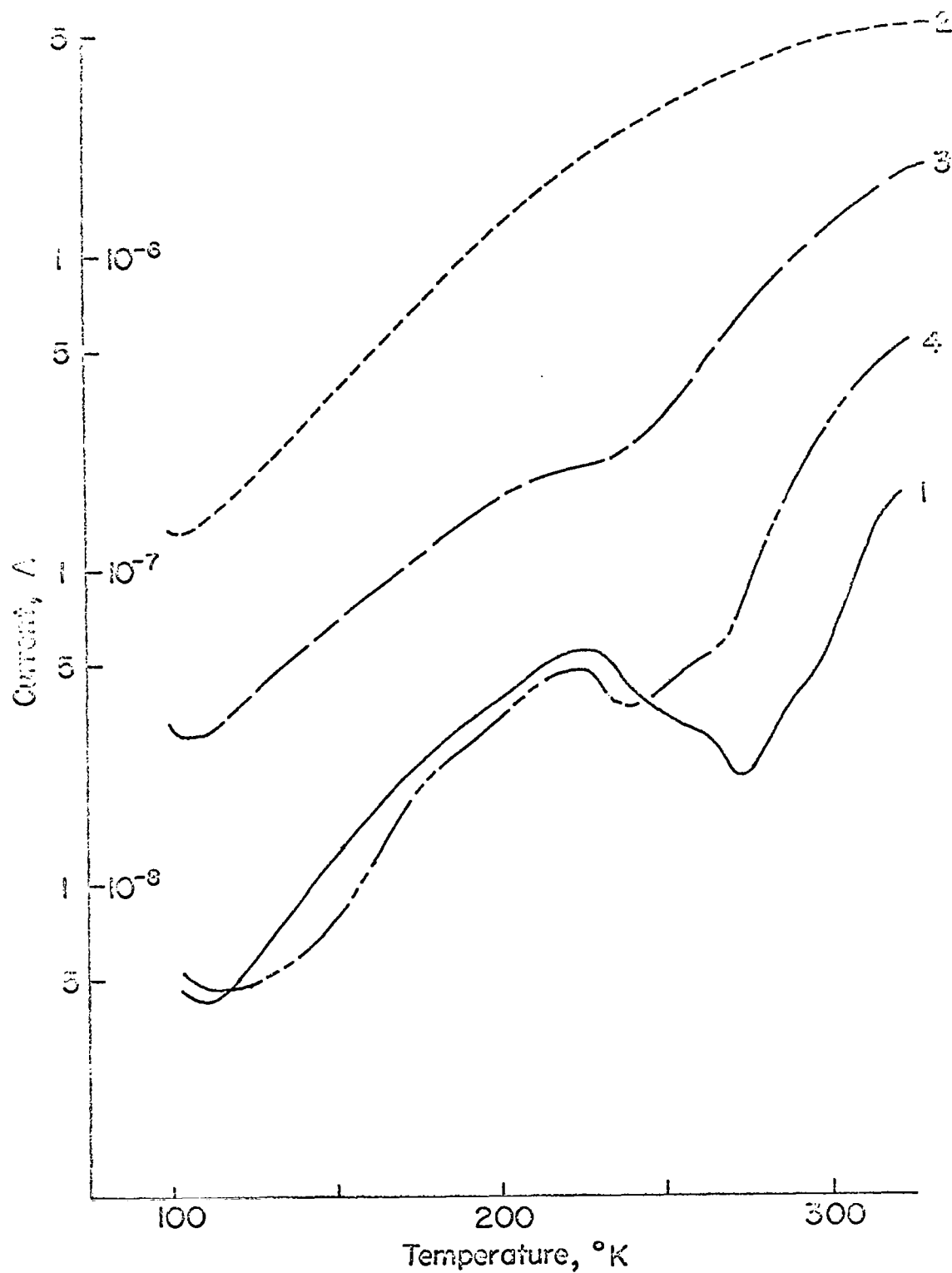


FIGURE 12: Thermally stimulated currents before and after X-irradiation at 200 keV from crystal C-4. Curve 1: Before irradiation. Curve 2: After irradiation. Curve 3: After 6 days at room temperature. Curve 4: Two months after irradiation.